DECOMPOSITION OF CALCIUM CARBONATE IN COCKLE SHELL

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ABSTRACT

Cockle shell or scientifically known as *Anadara granosa* is a local bivalve mollusc having a rounded shell with radiating ribs. The production of cockle shell in Malaysia was great and keeps increasing by year. In Malaysia, cockle shell was treated as waste with unpleasant smell and mostly left to natural deteriorates. Small number of study utilizes cockle shell as source of CaO. Hence, this study was conducted to propose a cockle shell as an alternative source of $CaCO_3$ by the calcination process. Calcination of $CaCO_3$ is a process of producing CaO which is subjecting a substance to the action of heat. This will done by using a muffle furnace. However, the efficiency of the process depends on the variable involved. Therefore, this paper aims to illustrate the effects of few variables on calcination reaction of $CaCO_3$ via thermal gravimetric analyzer (TGA) in order to optimize the process. In the present work, the vast availability of waste resources in Malaysia which is cockle shell were used as $CaCO_3$ sources. The experimental variables such as particle size, temperature and heating rate is put under study toward decomposition rate. The decomposition of calcium carbonate was investigated by using a particle size with 300, 425-600, and 1180μm in thermal gravimetric analyzer (TGA). The experiments were test with different temperature (700, 800 and 900°C) to study the decomposition rate of $CaCO_3$. Experiment has been conducted in inert atmosphere (N_2 gas). Analysis of XRF was conducted to determine the mineral composition of powder cockle shell. The surface morphology of raw cockle shell and calcined cockle shell was illustrated by SEM. Mineral composition of cockle shell by XRF showed that cockle shell was made up of 59.87% calcium (Ca). Thermal gravimetric data shows that smaller particle size experienced rapid weight loss compared to larger particle. The higher calcination temperature promotes higher calcination rate as this will increase the particles kinetic energy and thus, accelerates decomposition of $CaCO_3$ to CaO. The SEM analysis conclude that the higher calcination temperature give the structure of the sample more porous. Hence, more CO_2 will be released to give the more conversion to CaO.

ABSTRAK

Kerang atau saintifik dikenali sebagai Anadara granosa adalah moluska kerang tempatan mempunyai cengkerang bulat dengan terpancar tulang rusuk. Pengeluaran kerang di Malaysia adalah besar dan terus meningkat dari tahun ke tahun. Di Malaysia, kerang telah dianggap sebagai sisa dengan bau yang tidak menyenangkan dan kebanyakannya dibiarkan memburuk semula jadi. Sebilangan kecil kajian menggunakan kerang sebagai sumber CaO . Oleh itu, kajian ini telah dijalankan untuk mencadangkan kerang sebagai sumber alternatif bagi $CaCO_3$ oleh proses pengkalsinan ini. Pengkalsinan $CaCO_3$ adalah proses menghasilkan CaO yang menundukkan bahan untuk tindakan haba . Ini akan dilakukan dengan menggunakan relau meredupkan . Walau bagaimanapun, kecekapan proses yang bergantung kepada pemboleh ubah yang terlibat. Oleh itu , kertas ini bertujuan untuk menggambarkan kesan beberapa pembolehubah pada reaksi pengkalsinan $CaCO_3$ melalui terma penganalisis gravimetrik (TGA) untuk mengoptimumkan proses. Dalam karya ini, ketersediaan besar sumber air di Malaysia yang kerang telah digunakan sebagai sumber $CaCO_3$. Pembolehubah eksperimen seperti saiz zarah , suhu dan kadar pemanasan diletakkan di bawah kajian ke arah kadar penguraian. Penguraian kalsium karbonat telah disiasat dengan menggunakan saiz zarah dengan 300, 425-600 , dan 1.180 μm terma penganalisis gravimetrik (TGA). Eksperimen yang mengikuti ujian dengan suhu yang berbeza (700 , 800 dan 900 °C) untuk mengkaji kadar penguraian $CaCO_3$. Kajian dijalankan dalam suasana lengai (gas N) . Analisis XRF telah dijalankan untuk menentukan komposisi mineral kerang. Morfologi permukaan kerang mentah dan kerang calcined telah digambarkan oleh SEM. Komposisi mineral kerang dengan XRF menunjukkan bahawa kerang terdiri daripada 59.87 % kalsium (Ca). Data gravimetrik terma menunjukkan bahawa saiz zarah yang lebih kecil mengalami kehilangan berat badan yang cepat berbanding dengan zarah yang lebih besar . Suhu pengkalsinan yang lebih tinggi menggalakkan kadar pengkalsinan yang lebih tinggi kerana ini akan meningkatkan zarah tenaga kinetik dan dengan itu , mempercepatkan penguraian $CaCO_3$ untuk CaO . Analisis SEM membuat kesimpulan bahawa suhu pengkalsinan yang lebih tinggi memberikan struktur sampel lebih poros . Oleh itu, lebih banyak CO_2 akan dikeluarkan untuk memberi penukaran yang lebih untuk CaO.

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LIST OF ABBREVIATIONS

TGA	Thermal gravimetric analyzer
SEM	Scanning electron microscope
XRF	X-ray fluorescence
N_2	Nitrogen
CaO	Calcium oxide
$CaCO_3$	Calcium carbonate
CO_2	Carbon dioxide
Mg	Magnesium
P	Phosphorus
K	Potassium
Na	Sodium
°C	Degree celcius
μm	Micro meter
CS	Cockle shell
Ca	Calcium

1 INTRODUCTION

1.1 Background

Cockle shell or scientifically known as *Anadara granosa* is a local bivalve mollusc having a rounded shell with radiating ribs. In Malaysia, cockle shell as known as ‘kerang’ belonging to the family Arcidae (Awang et al., 2007). It is a cheap protein source which is quite common to be prepared as local dishes (Mohamed et al., 2012). Seashell contained of $CaCO_3$ which has enable it to be applied for quite a number of purpose such as biomaterial for bone repair (Awang et al., 2007) and also for industries and daily practice such as in waste water and sewage treatment, glass production, construction material, agricultural, and more. The industrial application of $CaCO_3$ are wide ranging, including paper, paints, ink, plastics, medicines, feedstuff, adhesives and rubbers (L. Xiang et al., 2005). $CaCO_3$ is one of the most abundant minerals in nature and has three polymorphs which is calcite, aragonite and vaterite (H. Bala et al., 2005). It’s found in muddy bottoms of coastal regions of South East Asian particularly Malaysia, Thailand and Indonesia. The history of cockle culture in Malaysia started in 1948 in Perak. Awang-Hazmi et.al had determined the mineral composition of *Anadara granosa* from from three major cultivation areas in West Coast of Peninsular Malaysia which are Penang, Kuala Selangor and Malacca. As reported in 2010, Malaysia had produced 78,024.70 metric tonnes of cockle for seafood industry (Izura and Hooi, 2008). 4000-5000 hectares of the west coast of Peninsular Malaysia were used for cockle culture (FAO, 2006). Chemical property analysis using x-ray fluorescene (XRF) shows cockle shell is made up of 97% Calcium (Ca) element and CaO is produced after decomposition was conducted (Mohamed et al.,2012).

Thermal decomposition of a cockle shell is called calcination. Calcination of $CaCO_3$ is a process of producing CaO – a widely used substances in high temperature applications (S. Yusup et al. 2012). Cockle shell decomposition is a gas-solid reaction in which the solid is the reactant. The reaction involves mass- and heat-transfer processes between a solid cockle shell particle and the calcination gas. The calcination of a cockle shell particle involves several steps, each of which is potentially rate-controlling. They are: (1) heat transfer from the bulk gas to the external surface and from the external surface to the reaction interface; (2) thermal decomposition of $CaCO_3$

at the reaction interface; and (3) mass transfer of CO_2 from the reaction interface to the bulk gas (Garcia-Labiano et al., 2002) . However, the efficiency of the process depends on the variable involved and the assumption made. Therefore, the effects of few variables on calcination reaction of $CaCO_3$ via thermo-gravimetric analyzer (TGA) was consider in order to optimize the process. In the present work, cockle shells were used as $CaCO_3$ sources. The experimental variables such as particle size and calcination temperature were employed.

1.2 Motivation and statement of problem

In Malaysia, cockle shell is abundantly available as a by-product from seafood industry and regarded as waste and mostly left at dumpsite to naturally deteriorate. According to L. Xiang et. al (2005), $CaCO_3$ is an abundant mineral comprising approximately 4% of the earth's crust. The study on thermal decomposition $CaCO_3$ has been extensively conducted in recent years (Garcia-Labiano et al., 2002). There are several sources of $CaCO_3$ for the production of CaO such as limestone, cement-kiln dust, seashells and more. Recent studies only focused on the use of shells from eggs, crabs, mussels and oysters as alternative sources for CaO. Although there are, in theory, many uses for shell, there is no singular solution to treat or utilise these materials as by-products and treated as waste. Nowadays, number of studies that utilize cockle shells as feedstock for CaO production is still limited. The common natural resources of $CaCO_3$ that have been applied this day are such as dolomite, limestone, magnesite, and also cement kiln dust. Industrial CaO is produced via thermal decomposition of calcium carbonate sources such as limestone which is obtained through mining and quarrying limestone hill. The most common CaO precursors are limestone and dolomite because of their availability and low cost. However, mining of these carbonate rocks will contribute to the environmental damage. The valorisation of cockle shells for the production of calcium carbonate has not activity performed at industrial level by the sector as the problem statement reported here, solely some specific literature describing a productive process of this type to get CaO. Therefore, cockle shells currently are found to be the best candidate as the alternative material as they made up of 95-99% by weight of $CaCO_3$. Only very recently, some initial studies were done to investigate the potential of this material. Cockle shell is a major financial and operational burden on the shellfish industry. Malaysia is having 1055 number of farmers working on cockle cultivation agriculture which involving 6000 hectare of cultivation area (Izura and

Hooi, 2008). However, these do not only indicate the vast availability of cockles but also the amount of waste shells generated.

The potential to exploit the vast availability of waste resources in Malaysia which is cockle shell as the potential biomass resources for $CaCO_3$ and CaO was great and lastly, converted to become the value added product. In Malaysia, the shells are treated as waste and mostly left at dumpsite to naturally deteriorate. The shells that been dumped and left untreated may cause unpleasant smell and disturbing view to the surrounding. Thus, in this study, cockle shells were chosen as the new potential source of CaO instead not using other sources of $CaCO_3$. Hence, it can use as the potential source of CaO. Cockle shells which are rich in minerals content such as Ca, C, Mg, P, K, Na and more was suitable for the purposes of industries and daily practice. The experimental variables such as calcination temperature and particle sizes were put under study in order to optimize the calcination process. As Malaysia is rich in waste cockle shells, and also the production of cockle shell was great by year, the potential to exploit them for the production of CaO is great. Hence this program aims to utilise the $CaCO_3$ in cockle shell as new potential source of CaO. This project helps meet the medium term objective for cockle shells by raising awareness of possible ways to generate economic return from waste and in the development of a regional approach to facilitate further development.

1.3 Objective

The following are the scope of this research:

- To propose cockle shell as new potential source for calcium oxide, CaO.

1.4 Scope of this research

The following are the scope of this research:

- Use calcination process to produce CaO.
- Characterize the minerals content in cockle shell.
- Study the effect of temperature and particle size to produce CaO from cockle shell

1.5 Main contribution of this work

The following are the contributions

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 presented the background of this study, objective of this research, scope of research and the main contribution of this research. This will including the background of cockle shell, uses of $CaCO_3$ in industrial applications, cockle shell decomposition and also mass and heat transfer process in cockle shell decomposition.

Chapter 2 presented the overview of how the study has been analyzed including the type of cockle shell, the availability of cockle shell which is the main material going to be use in this study. The process on how the CaO can be synthesized from cockle shell also include in this chapter. This will including the review on calcination process and the condition on calcination, This chapter will also including the comparison of previous work from any researchers.

Chapter 3 presented the overall method of calcination process. The preparation of material, characterization of cockle shell, research flow diagram, and also the equipments used which are thermal gravimetric analyzer (TGA), x-ray fluorescence (XRF), furnace, sieve shaker, and scanning electron microscope (SEM) were also presented in this chapter. This chapter shows the presented work on how to get the main product which is CaO.

Chapter 4 presented the results and discussion from what the research have been done. In this chapter, the comparison of this work from previous study has been analyzed. Analysis of mineral content in cockle shell, analysis on thermal gravimetric analyzer, and the surface morphology of cockle shell all were discussed in this chapter.

2 LITERATURE REVIEW

2.1 Overview

This section is divided into two parts and describes prior theoretical and experimental work related either directly to calcium carbonate decomposition or to gas-solid reactions in general, restricted only to their bearing on the reaction being studied. The largest part of this section is devoted to a review of the experimental literature on calcium carbonate decomposition. It is interesting to note that the rich literature on calcium carbonate decomposition appears to be driven by theoretical considerations. The other part also included the background of seashell, cockle shell and also calcination process.

2.2 Sea shell

Seashells are the external skeletons of a class of marine animals called Mollusks. It is composed largely of $CaCO_{3.}$ Typical seashells are composed of two distinct layers, with an outer layer made of calcite (a hard but brittle material) and an inner layer made of a tough and ductile material called nacre. Nacre is a biocomposite material that consists of more than 95% of tablet shape aragonite, CaCO3, and a soft organic material as matrixSeashells are quite well developed and applied to other countries for various purposes. The chemical composition of shells is >90% $CaCO_3$ by weight (Falade, 1995; Yoon et al., 2003, 2004; Yang et al., 2005; Ballester et al., 2007; Mosher et al., 2010). There are various type of sea shell including short-necked clamp, oyster, green mussel, scallop shell and cockle. $CaCO_3$ content can be used for various purpose including plastics, medicines, paints and more. In the case of molluscs, the processing installations generate significant amounts of shell waste that account for more than 80,000 tons a year and could be recovered by different methods in an environmentally sound manner (Barros et al., 2009).

Mollusks are marine animals that have a very soft body . Various dangerous factors, e.g., attacks from fishes or other predators or impact from a falling rock continuously threatens their soft tissues. Nature has wisely devised a suitable protection for mollusks in the form of a hard ceramic layer known as a seashell or simply a shell. To this date, about 60,000 species of mollusk shells have been found in nature, with a great variety of shell sizes and shapes. Mollusk shells are categorized into several classes but most mollusk species fall within three main categories: bivalves, gastropods and cephalopods (Figure 2-1). Complicated spiral-like shapes are found in cephalopod class whereas bivalve and gastropod shells possess simpler shapes.

(a) bivalve (b) gastropods (c) cephalopods

Figure 2-1: Categories of mollusc

Several attempts were made to capture the shapes of seashells using mathematical formulations (V. Helm et al., 1998). In addition to shape, seashells exist in a variety of sizes starting from less than 1 mm (micromollusks) up to 25 cm in shell of abalone. The strength of shells is a function of the shape and the size of the shell, and of the materials it is made of. Depending on the living environment of the mollusc shells, various types of loading may be applied on the shell structure. For instance, seashells are prone to an impact load from the falling of rocks, attacks from other marine animals such as sharks and crabs or hydrodynamics loads of high-energy environments. The shell structure is adapted to that living condition to withstand feasible threats from nature. Excessive mechanical load will of course break the shell, following failure patterns which also depend on the structure and geometry of the shell. In the case of a sharp penetration, the shell may fracture only in a small region of the structure while the other parts remain intact. On the other hand, distributed loading may crush the shell into several pieces. Zuschin (2002) performed numerous compressive and compaction experiments on three seashell species, i.e., Mercenaria mercenaria, Mytilus edulis and Anadara ovalis, to obtain their strength, failure pattern and the predictor parameter on the strength of the shell. Among all the structural and geometrical parameters of the shell, shell thickness was revealed to be the most significant predictor of the shell strength.

As simplified in Table 2-1, Barros et al. (2009) described that seashells are quite well developed and applied in other countries for various purposes. In Malaysia recently, it was found that cockles shell is the potential biomass resource for bone repair material especially made for cancer patients (Mokhtar., 2009).

Table 2-1: Application of seashell in other countries

Type of seashell	Country	Application
Oysters	Japan	Cement clinkers
	Korea	Fertilizers, water eutrophication
Scallops	UK	Construction road forestry
	Peru	Obtain lime as the input for other industrial sector
Mussels	Spain	Animal feed additives, liming agent, constituent
	US	fertilizers
	Holland	Soil conditioner, liming agent
		Mussel tiles

Source: Barros et al. (2009)

2.3 *Cockle shell*

Anadara granosa or locally known as 'kerang' is a local bivalve molluscs (Faridah and Nurul, 2008). A cockle 'Kerang', is a common edible European bivalve mollusc, having a rounded shell with radiating ribs. Anadara granosa locally known as kerang in Malaysia is a bivalve belonging to the family Arcidae (Awang et al., 2007). It contained almost 95-99% by weight of $CaCO_{3.}$ Cockles are composed of two distinct material. The shell consists of calcium carbonate in the form of aragonite, calcite and vaterite. In Malaysia, cockle shell is abundantly available as a by-product from seafood industry. It is a cheap protein source which is quite common to be prepared as local dishes (Mohamed et al., 2012). *Anadara granosa*, is also an important of protein source. It's found in muddy bottoms of coastal regions of South East Asian particularly Malaysia, Thailand and Indonesia.

According to L. Xiang et.al (2005), $CaCO_3$ is an abundant mineral comprising approximately 4% of the earth's crust. The industrial application of $CaCO_3$ are wide ranging, including paper, paints, ink, plastics, medicines, feedstuff, adhesives and rubbers (L. Xiang et al., 2005). Although there are, in theory, many uses for shell, there is no singular solution to treat or utilise these materials as by-products and treated as waste. Li et al. (2009) found that the composition of CaO in sea shells is higher compared to other naturally occurring sources such as limestone as indicated in Table 2-2. The combination of Li's result and other similar findings such as scallop shells, sea shells and crab crust and legs (Sasaki et al., 2002; Jeon and Yeom, 2009) on the composition of calcium-based compound in marine shells justifies the use of cockle shells as a potential biomass for $CaCO_3$-based resources.

Table 2-2: Comparison of oxides content in seashell and limestone

Sample	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	Na_2O	Others
MV Shell	52.41	0.22	0.11	0.07	0.17	0.37	0.33
Mussel shell	50.45	0.18	0.78	0.09	0.12	0.24	0.82
Scallop shell	54.53	0.27	0.00	0.04	0.16	0.49	0.47
MM limestone	48.83	4.8	2.76	0.28	0.54	0.02	0.36
JN limestone	50.28	2.54	4.21	0.51	0.95	0.01	0.32

Source: Li et al. (2009)

The study on thermal decomposition $CaCO_3$ has been extensively conducted in recent years (Garcia-Labiano et al., 2002). There are several sources of $CaCO_3$ for the production of CaO such as limestone, cement-kiln dust, seashells and more. Recent studies only focused on the use of shells from eggs, crabs, mussels and oysters as alternative sources for CaO. Nowadays, number of studies that utilize cockle shells as feedstock for CaO production is still limited. In Malaysia, the shells are treated as waste and mostly left at dumpsite to naturally deteriorate. In this study, cockle shells were chosen as the new potential source of CaO instead not using other sources of $CaCO_3$. Hence, it can use as the potential source of CaO. Cockle shells which are rich in minerals content such as Ca, C, Mg, P, K, Na and more was suitable for the purposes of industries and daily practice. Seashell contained of 95-99% by weight of $CaCO_3$ which has enable it to be applied for quite a number of purpose (Barros et al., 2009 ; Nakatani et al., 2009). As Malaysia is rich in waste cockle shells, the potential to exploit them for the production of CaO is great. Chemical property analysis using x-ray fluorescene (XRF) shows cockle shell is made up of 97% Calcium (Ca) element and CaO is produced after decomposition was conducted (Mohamed et al.,2012).

2.3.1 Production of cockle shell in Malaysia

The history of cockle culture in Malaysia started in 1948 in Perak. Awang-Hazmi et.al had determined the mineral composition of Anadara granosa from three major cultivation areas in West Coast of Peninsular Malaysia which are Penang, Kuala Selangor and Malacca. In 2006, Malaysia had produced 45,674.58 metric tonnes of cockle for seafood industry (Izura and Hooi, 2008). 4000-5000 hectares of the west coast of Peninsular Malaysia were used for cockle culture (FAO, 2006).

Cockle shell is a major financial and operational burden on the shellfish industry. Malaysia is having 1055 number of farmers working on cockle cultivation agriculture which involving 6000 hectare of cultivation area (Izura and Hooi., 2008). However, these figures do not only indicate the vast availability of cockles but also the amount of waste shells generated. The shells that been dumped and left untreated may cause unpleasant smell and disturbing view to the surrounding. Hence this program aims to utilise the $CaCO_3$ in cockle shell as new potential source of CaO. Cockle shell has to undergo calcination process– a widely used substances in high temperature applications. This project helps meet the medium term objective for cockle shells by raising awareness of possible ways to generate economic return from waste and in the development of a regional approach to facilitate further development. Figure 2-2 indicates the production of cockle shell in Malaysia from 2005 to 2012 (Annual Fisheries., 2012). Based on this statistic, the production of cockles started to decline from 2010 till 2012 due to limited suitable culture area for expansion in Peninsular Malaysia and inadequate spat-fall areas in Sabah and Sarawak. Higher operational costs and reduction of mangrove areas that helps to supply the cockle seeds also contribute towards the decline in cockles' production. However, Malaysia expected to produce 130,000 tons of cockles during the Ninth Malaysia Plan. Thus to realize the target, several steps had been recommended such as reserving and gazetting spatfall areas, reducing operational costs, and increasing research on development of more spat-fall areas. Table 2-3 shows that production of cockle shell (tonnes) by state in Malaysia from year 2005 to 2012.

Table 2-3: Cockle production (tonnes) by states in Malaysia

Year	**Kedah**	**Penang**	**Perak**	**Selangor**	**Johor**	**Total**
2005	232.04	10,991.65	37,415.73	9,398.48	1,477.95	59,515.85
2006	69.70	11,597.11	31,512.42	1,827.00	668.26	45,674.49
2007	132.91	12,670.42	33,711.51	3,021.32	84.00	49,620.16
2008	170.70	12,675.25	33,403.55	14,750.50	138.32	61,138.32
2009	651.70	6,762.50	26,702.77	30,742.43	56.98	64,916.38
2010	1,295.39	8,886.39	26,387.36	41,410.06	45.50	78,024.70
2011	659.19	7,682.27	21,759.37	26,505.53	938.04	57,544.40
2012	389.97	7,737.34	22,068.56	11,842.66	93.50	42,132.03

Source: Annual Fisheries (2012)

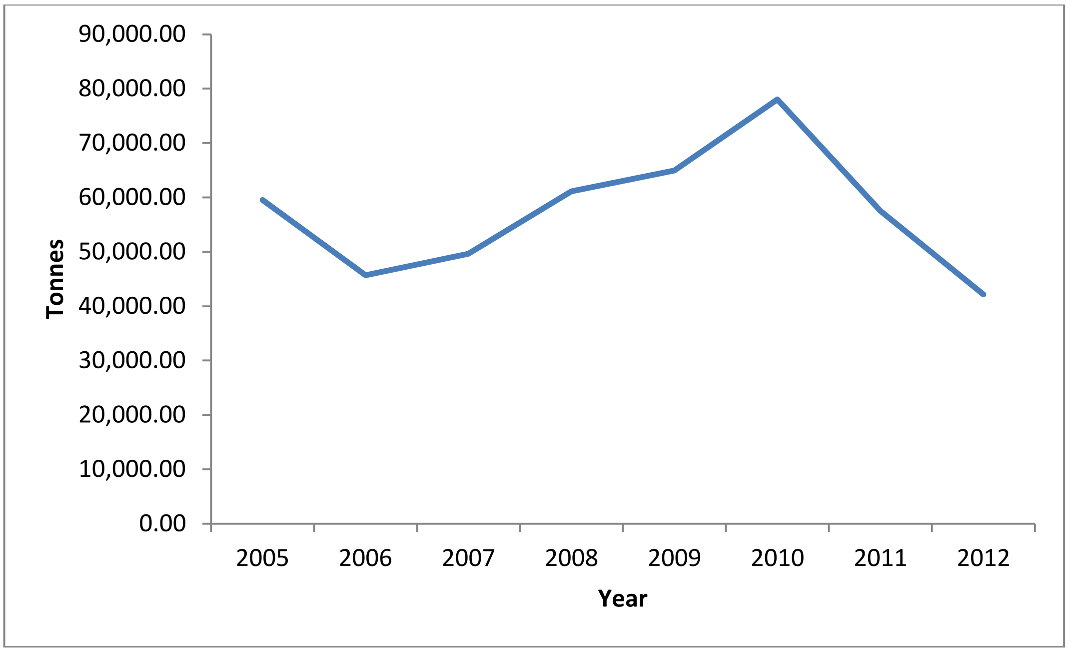

Figure 2-2: Production of cockle shell in Malaysia

There are over 200 living species known. They are categorised into six groups well-known in the world (see Table 2-4) which are Vongole, Pipi (Donax deltoids), Surf clam (Dosinia caerulea), Sydney cockle (Anadara trapezius), Blood cockle (Kerang) and Razor clam (Pinna bicolor).

Table 2-4: Types of cockles

Groups of cockle	**Description**
Vongole	Members of the venus shell family. Found around the southern Australian coast from Fraser Island in Queensland to Cape Leeuwin in WA (including Tasmania) and harvested from sheltered or sandy subtidal sediment of tidal flats and estuary mouths. Known as sand cockle
Pipi (Donax deltoids)	Its smooth, wedge-shaped, cream to pale brown shell can sometimes be slightly yellow or green and have pinky-purple bands and averages 5-6 cm in diameter. Mainly hand-harvested from the intertidal zone of sandy surf beaches.

Surf clam (Dosinia caerulea)	Its rough, circular shell. About 3-4.5 cm in diameter. Varies in colour from cream through greyish white or pale yellow to light brown and has sculpted, concentric ridges. Found in the Mediterranean.
Sydney cockle (Anadara trapezius)	Its shell can be up to 8 cm in diameter and has prominent, outward-radiating ribs. Found in estuaries, mud flats and seagrass beds.
Blood cockle (Kerang)	It named for the reddish liquid released when it opened and sometimes reddish tinge of its shell, which is usually about 6 cm in diameter. Found intertidally in northern Australia, eastern Asia such Indonesia and Malaysia.
Razor clam (Pinna bicolor)	Called razor fish. Has a long narrow shell, roughly the shape of an old-fashioned cutthroat razor and is harvested in sand or mud near the low water mark on very sheltered bays in SA.

Artificial reef is a structure that is submerged in the sea or rivers; used to preserve and promote the breeding of marine life. In Malaysia, this method has proven effective since it was introduced in the early 70s (Chou, 1997). Each year, the government has allocated a large budget in supporting this continuous effort to increase marine productivity and benefit the eco-tourism in the country. In 2009 alone, the government has approved RM15 million in the second economic stimulus package for artificial reefs development (Fauzi, 2009). Basically, any materials that are dumped into the water can be defined as artificial reef. Waste products such as used tyres, old vehicles and refrigerator have been used for cheap option of artificial reef which is considered as one form of pollution. If these materials do not manage properly, it can cause adverse impact to the environment. Another option for artificial reef is concrete structures. It could be higher in cost but their ability of being easily constructed according to various configurations and its durability has made them increasingly used for artificial reefs (Chou, 1997).Studies on cockle shell as part of the construction material for artificial reef is relatively new. The potential of the shell in concrete composite has not yet been exploited. The shell is chosen due to its properties that suggest the material compatibility to be applied for the purpose. Thus, this study focused on exploration and experimentation of integrating cockle shells in the construction of concrete artificial reefs as an eco-friendly and economic alternative.

2.4 Characterization of cockle shell

2.4.1 Surface morphology

The morphology of raw cockle shell and calcined cockle shell at 700, 800, and 900°C was examined by SEM (Figure 2-3). The natural shell displays a typical layered architecture. With the calcination temperature rising from 700 to 900°C, the microstructures of natural shell are changed significantly from layered architecture to porous structure. The calcined cockle shells were irregular in shape, and some of them bonded together as aggregates. However, the smaller size of the grains and aggregates could provide higher specific surface areas. Since all samples are considered to be less-porous or even nonporous, the size of the particle should directly respond to the surface area. There are three crystal structure of $CaCO_3$ which is aragonite, calcite and vaterite.

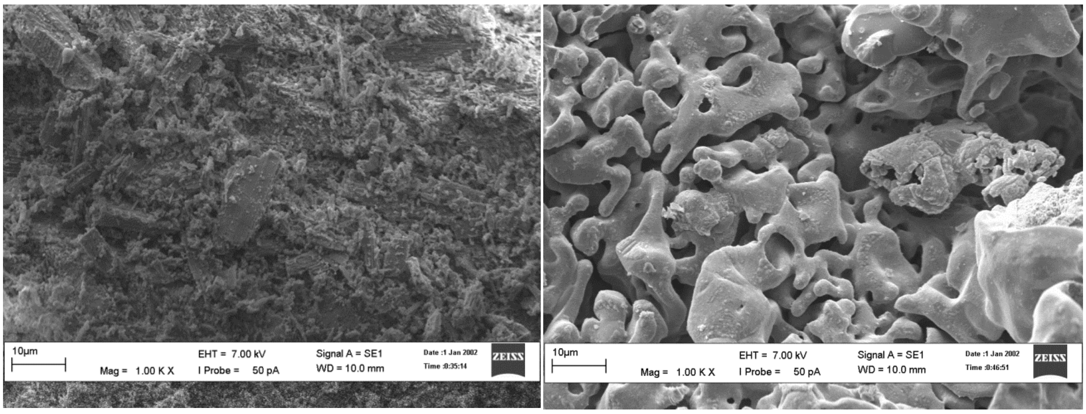

Figure 2-3: Surface morphology of cockle shell

Based on the XRF and SEM results on previous study, the composition of cockle shell is proven to be rich in calcium and presence of CaO is detected in calcined cockle shells (Mohamed et al., 2012). The findings agree with Li et al. (2009) which shows high amount of calcium in shells. Based on XRD spectra, raw cockle shells contain aragonite $CaCO_3$ which is one of the orthorhombic polymorphs of $CaCO_3$ other than calcite and veterite. Despite its relative instability, aragonite is still the most suitable compound for CaO production compared to the calcite or veterite. The shells form this by-product industry are treated as waste and mostly left at dumpsite to naturally deteriorate. It is hard to dispose due to its strong property. The application of this material is still very limited although there is an attempt to use it in craft production. Only very recently, some initial studies were done to investigate the potential of this material.

2.4.2 Mineral content in cockle shell

The X-ray fluorescence (XRF) analyses provide the mineral compositions of the cockle shell. The mineral composition reported as element of cockle shell. Previous study shows that cockle shell were made up of $CaCO_3$, which is one of the sources of CaO. Recent report study by Zuki et al. (2004) stated that the mineral composition of Anadara granosa is almost similar to that of coral. Thus, the finding suggests the possibility of using cockle shell as alternative biomaterials for production of CaO. From previous study done by Zuki et al, almost 98.68% of CaC content in cockle shell. Awang-Hazmi et al who also performed mineral composition cockle shell determine that 98.70% of CaC. Meanwhile, S.Yusup et al also determine that mineral content in cockle shell contained 98.99% of CaC content in cockle shell. Table 2-5 illustrated mineral composition from previous study.

Table 2-5: Minerals content in cockle shell

Author / **Minerals (%wt)**	**CaC**	**Mg**	**Na**	**P**	**K**	**Other**
Zuki et al	98.68	0.20	0.87	0.02	0.04	0.20
Awang-Hazmi et al	98.70	0.05	0.9	-	-	<0.1
S.Yusup et al	98.99	0.51	-	-	-	<0.1

2.5 Uses of calcium carbonate ($CaCO_3$)

Although there are many different uses for calcium carbonate, the production are still very limited. There are many other uses for calcium carbonate ranging from the manufacturing process for fibre glass to pigmenting paint. Calcium carbonate makes up about 20 percent of the pigments used in the paint industry. Calcium carbonate is used to extend the resin or polymers because of its controlled colour and low cost. Calcium carbonate also is used to control the sheen or gloss in flat paints. Seashell contained of 95-99% by weight of $CaCO_3$ which has enable it to be applied for quite a number of purpose (Barros et al., 2009 ; Nakatani et al., 2009). Previous study in Malaysia has showed that this material has potential as biomaterial for bone repair (Awang et al., 2007). The suitability of cockle shell as calcium-based adsorbent is confirmed by its high calcium content, as reported by Awang-Hazmi et al. Calcium oxide is recognized as an efficient carbon dioxide adsorbent and separation of CO_2 from gas stream using CaO based adsorbent is widely applied in gas purification process especially at high temperature reaction (Mohamed et al., 2012). CaO which is used in industries and daily practice such as in waste water and sewage treatment, glass production, construction material, agricultural, and more. In various studies of other seashell types like oysters, scallops and mussels revealed that they are quite well developed and applied indiverse industry around the world for fertilizers, construction materials, cement clinkers and tiles (Barros, 2004). The paper industry is a major consumer of mineral pigments. In paper coating applications, calcium carbonate, fine ground from 0.5 to 3.5 microns (the average width of a human hair is 100 microns), is used to make a whiter, brighter sheet. In paper filling applications, calcium carbonate can improve the whiteness of the sheet and reduce costs by replacing expensive fiber and pigments. The chemical properties of calcium carbonate are used to produce non-acidic paper.

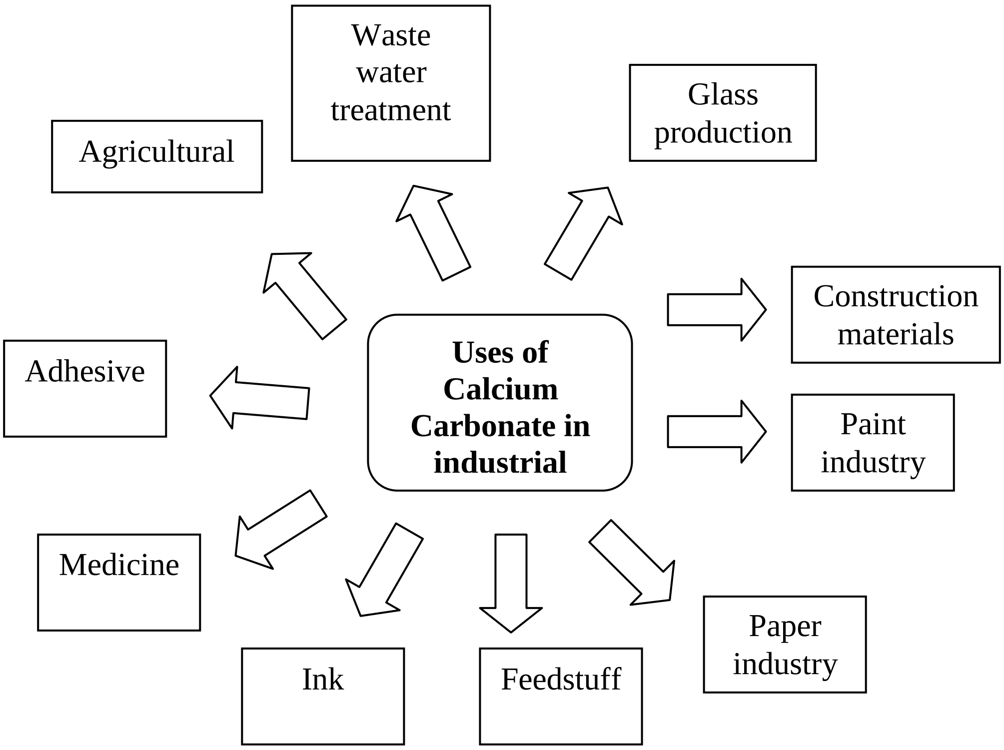

Figure 2-4: Uses of calcium carbonate in industrial application

2.6 Review of cockle shell calcination studies

According to Yan et al. (2010), calcination is described as a five-step process which involves (i) heat transfer from surrounding to external surface of particle, (ii) heat transfer from exterior surface to interior samples interface, (iii) heat absorption and thermal decomposition at the interface layer, (iv) diffusion of formed CO_2 through porous layer of calcium oxide (CaO) and (v) diffusion of CO_2 towards the surrounding.

The importance calcination performance is in two aspects:

(1) Calcination kinetics, which determine the time required for calcination

(2) The physical structure change during calcination, which determines the reactivity of the CaO produced.

Calcination of cockle shell has been studied extensively. Decomposition equilibrium, chemical kinetics, the microstructure of the calcine, and the transport processes associated with the calcination have been investigated by numerous researchers1'98. However, most studies have been conducted on the calcination of cockle shell particles at lower calcination temperatures. Relatively less work has been conducted on the calcination of small particles at high calcination temperatures.

Therefore, for reasons of both practical interest and fundamental understanding, it was timely to study the calcination of small particles under high temperature, short residence time conditions. The focus of this study was, therefore, the calcination behavior of cockle shell under conditions using the furnace. Particle sizes of 0.3, 0.4-0.6, and 1.2 mm and temperatures of 700, 800, and 900°C were used. Naturally occurring cockle shell exist in different varieties, each having a unique physical structure and chemical composition. An extensive review of the different types of shell has been given by (Boynton et al).

$CaCO_3$ can be generally found in three distinct crystalline phases *i.e.* calcite, aragonite and vaterite (shown in Figure 2-5). Calcite is the most stable and most commonly found in nature. Aragonite, however, can only be found in precipitate $CaCO_3$ or seashells whereas vaterite is found from synthesized $CaCO_3$ and does not occur naturally. The crystallized form of $CaCO_3$ is called a calcite. Together with this major constituent, naturally occurring cockle shell also contain some impurities (quartz, clay and trace elements), with total amounts ranging from less than 1 to up to 2.0 %.

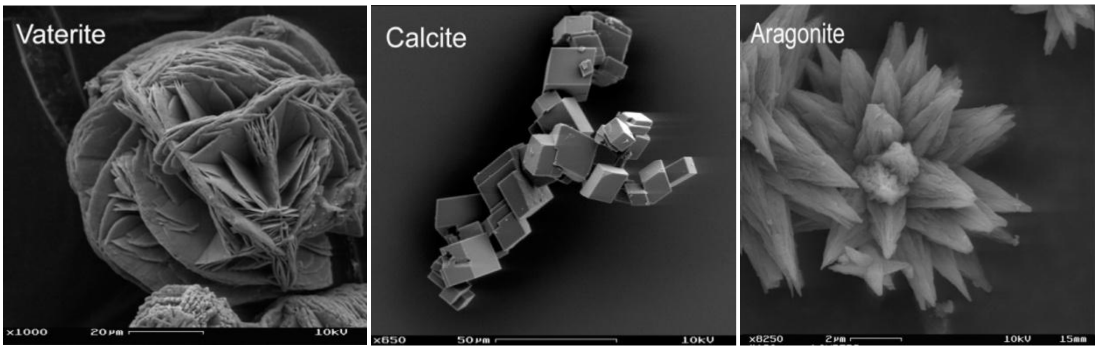

Figure 2-5: Crystal structure of calcium carbonate

Thermal decomposition of a cockle shell is called calcination. The calcination of cockle shell is through the endothermic reaction $CaCO_3 \leftrightarrow CaO + CO_2$. If the partial pressure of CO_2 is less than the equilibrium value, the reaction will proceed. The equilibrium decomposition pressure of CO_2 as a function of the decomposition temperature is shown in Figure 2-6. Good agreement on calcite decomposition equilibrium has been reached among various researchers. The calcination of cockle shell involves single steps. The only step is the decomposition of the calcium carbonate $CaCO_3 \leftrightarrow CaO + CO_2$. A review of this study is given by Bandi and Krapf. The equilibrium decomposition temperature has been reported to be in the range of 893 to 1,073 K, depending on the CO_2 partial pressure and the experimental conditions, and no